

THE CLAIMS

What is claimed is:

1. Large-area, single-crystal semi-insulating gallium nitride.
2. Gallium nitride according to claim 1, doped with a transition metal dopant species to compensate residual donor species in the gallium nitride, wherein the concentration of transition metal dopant species is sufficient to render the gallium nitride semi-insulating.
3. Gallium nitride according to claim 2, wherein the transition metal dopant species comprises at least one transition metal selected from the group consisting of Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd and Hg.
4. Gallium nitride according to claim 2, wherein the transition metal dopant species comprises at least one transition metal selected from the group consisting of Mn, Fe, Co, Ni and Cu.
5. Gallium nitride according to claim 2, wherein the transition metal dopant species comprises manganese.
6. Gallium nitride according to claim 2, wherein the transition metal dopant species comprises cobalt.
7. Gallium nitride according to claim 2, wherein the transition metal dopant species comprises nickel.
8. Gallium nitride according to claim 2, wherein the transition metal dopant species comprises copper.
9. Gallium nitride according to claim 2, wherein the transition metal dopant species comprises iron.

10. Gallium nitride according to claim 1, as formed by hydride vapor phase epitaxy (HVPE).
11. Gallium nitride according to claim 1, with a thickness in a range of from about 50 micrometers to about 5 centimeters.
12. Gallium nitride according to claim 1, in the form of a boule.
13. Gallium nitride according to claim 12, wherein the boule has a thickness in a range of from about 300 micrometers to about 5 centimeters.
14. Gallium nitride according to claim 1, which is free-standing.
15. Gallium nitride according to claim 14, having a diameter of at least 50 millimeters, and a thickness of at least 300 micrometers.
16. Gallium nitride according to claim 15, wherein the thickness is in a range of from 300 micrometers to 5 centimeters.
17. Gallium nitride according to claim 1, having a resistivity greater than about $10^2 \Omega\text{-cm}$, at 25°C .
18. Gallium nitride according to claim 1, having a resistivity greater than about $10^5 \Omega\text{-cm}$, at 25°C .
19. Gallium nitride according to claim 1, having a resistivity greater than about $10^2 \Omega\text{-cm}$, at 200°C .
20. Gallium nitride according to claim 1, having a resistivity greater than about $10^5 \Omega\text{-cm}$, at 200°C .
21. Gallium nitride according to claim 1, having a resistivity greater than about $10^5 \Omega\text{-cm}$, at 300°C .

22. Gallium nitride according to claim 1, wherein unintentional impurities are less than $5 \times 10^{17} \text{ cm}^{-3}$.
23. Gallium nitride according to claim 1, wherein unintentional impurities are less than $1 \times 10^{17} \text{ cm}^{-3}$.
24. Gallium nitride according to claim 1, wherein unintentional impurities are less than $5 \times 10^{16} \text{ cm}^{-3}$.
25. Gallium nitride according to claim 1, wherein unintentional impurities are less than $1 \times 10^{16} \text{ cm}^{-3}$.
26. Gallium nitride according to claim 1, having a dislocation defect density not exceeding 10^7 defects / cm^2 .
27. Gallium nitride according to claim 1, having a dislocation defect density not exceeding 10^6 defects / cm^2 .
28. Gallium nitride according to claim 1, having a dislocation defect density not exceeding 10^5 defects / cm^2 .
29. Gallium nitride according to claim 2, comprising background impurities including silicon and oxygen, wherein said transition metal dopant species comprises iron, and said iron has a concentration that is greater than total concentration of said silicon and said oxygen.
30. Gallium nitride according to claim 2, wherein said transition metal dopant species comprises iron, at a concentration in a range of from about 3×10^{16} atoms/ cm^3 to about 7×10^{17} atoms/ cm^3 , as determined by SIMS.

31. Gallium nitride according to claim 1, doped with a dopant species to compensate residual donor species in the gallium nitride, wherein the dopant species has an activation energy greater than 0.35 eV.
32. Gallium nitride according to claim 1, doped with a dopant species to compensate residual donor species in the gallium nitride, wherein the dopant species has an activation energy greater than 0.50 eV.
33. Gallium nitride according to claim 1, doped with a dopant species to compensate residual donor species in the gallium nitride, wherein the dopant species has an activation energy greater than 0.75 eV.
34. Gallium nitride according to claim 1, doped with a transition metal dopant species having an activation energy greater than 0.35 eV.
35. Gallium nitride according to claim 1, including microelectronic circuitry fabricated thereon and/or therein, wherein the gallium nitride is semi-insulating in an operating temperature regime of said microelectronic circuitry.
36. Gallium nitride according to claim 1, having electronic circuitry fabricated thereon and/or therewithin.
37. An electronic device structure, comprising gallium nitride as in claim 1, and an electronic device fabricated thereon and/or therewithin.
38. The electronic device structure of claim 37, wherein the electronic device comprises a high electron mobility transistor (HEMT).
39. The electronic device structure of claim 37, wherein the electronic device comprises a monolithic microwave integrated circuit (MMIC).
40. The electronic device structure of claim 37, wherein said gallium nitride is on a conductive substrate.

41. The electronic device structure of claim 40, wherein the electronic device comprises a high power rectifier.
42. A method of forming large area, semi-insulating gallium nitride, comprising growing gallium nitride material by a growth process, and during the growth process, doping the growing gallium nitride with a dopant species that is effective to compensate residual donor species in the gallium nitride, wherein the concentration of the dopant species is sufficient to render the gallium nitride semi-insulating.
43. The method of claim 42, wherein the dopant species comprises at least one transition metal selected from the group consisting of Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd and Hg.
44. The method of claim 42, wherein the dopant species comprises at least one transition metal selected from the group consisting of Mn, Fe, Co, Ni and Cu.
45. The method of claim 42, wherein the dopant species comprises manganese.
46. The method of claim 42, wherein the dopant species comprises cobalt.
47. The method of claim 42, wherein the dopant species comprises nickel.
48. The method of claim 42, wherein the dopant species comprises copper.
49. The method of claim 42, wherein the dopant species comprises iron.
50. The method of claim 42, wherein the gallium nitride contains background impurities including silicon and oxygen, wherein said dopant species comprises iron, and said iron has a concentration that is greater than total concentration of said silicon and said oxygen.
51. The method of claim 42, wherein said dopant species comprises iron, and the growth process is conducted to provide the gallium nitride with an iron concentration in

a range of from about 3×10^{16} atoms/cm³ to about 7×10^{17} atoms/cm³, as determined by SIMS.

52. The method of claim 42, wherein the growth process comprises hydride vapor phase epitaxy (HVPE).

53. The method of claim 42, wherein the gallium nitride has a resistivity greater than about 10^2 Ω-cm, at 25°C.

54. The method of claim 42, wherein the gallium nitride has a resistivity greater than about 10^5 Ω-cm, at 25°C.

55. The method of claim 42, wherein the gallium nitride has a resistivity greater than about 10^2 Ω-cm, at 200°C.

56. The method of claim 42, wherein the gallium nitride has a resistivity greater than about 10^5 Ω-cm, at 200°C.

57. The method of claim 42, wherein the gallium nitride has a resistivity greater than about 10^5 Ω-cm, at 300°C.

58. The method of claim 42, wherein the dopant species has an activation energy greater than 0.35 eV.

59. The method of claim 42, wherein the dopant species has an activation energy greater than 0.50 eV.

60. The method of claim 42, wherein the dopant species has an activation energy greater than 0.75 eV.

61. The method of claim 42, wherein unintentional impurities of the gallium nitride are less than 5×10^{17} cm⁻³.

62. The method of claim 42, wherein unintentional impurities of the gallium nitride are less than $1 \times 10^{17} \text{ cm}^{-3}$.

63. The method of claim 42, wherein unintentional impurities of the gallium nitride are less than $5 \times 10^{16} \text{ cm}^{-3}$.

64. The method of claim 42, wherein unintentional impurities of the gallium nitride are less than $1 \times 10^{16} \text{ cm}^{-3}$.

65. The method of claim 42, wherein the gallium nitride has a dislocation density not exceeding 10^7 defects / cm^2 .

66. The method of claim 42, wherein the gallium nitride has a dislocation density not exceeding 10^6 defects / cm^2 .

67. The method of claim 42, wherein the gallium nitride has a dislocation density not exceeding 10^5 defects / cm^2 .

68. The method of claim 42, wherein the gallium nitride produced by the growth process is free-standing.

69. The method of claim 68, wherein the gallium nitride has a diameter of at least 50 millimeters, and a thickness of at least 300 micrometers.

70. The method of claim 69, wherein the gallium nitride has a thickness in a range of from 300 micrometers to 5 centimeters.

71. The method of claim 42, comprising growing the gallium nitride to form a boule by an HVPE growth process.

72. The method of claim 42, further comprising fabricating electronic circuitry on and/or within the gallium nitride.

73. The method of claim 42, further comprising fabricating an electronic device on and/or within the gallium nitride.

74. The method of claim 42, comprising forming said gallium nitride on a conductive substrate.

75. The method of claim 42, wherein said growth process comprises growing gallium nitride on a seed crystal.

76. The method of claim 75, wherein the seed crystal comprises a free-standing GaN seed crystal.

77. The method of claim 75, wherein said growth process comprises growing gallium nitride on a conductive seed crystal, said method further comprising removing the conductive seed crystal from the gallium nitride produced by the growth process.

78. The method of claim 75, wherein the seed crystal comprises a semi-insulating seed crystal.

79. The method of claim 75, wherein the seed crystal comprises a seed crystal having a defect density of less than 10^7 defects/cm².

80. The method of claim 42, wherein the growth process comprises reacting hydrochloric acid (HCl) with metallic gallium to form gaseous GaCl, and reacting the gaseous GaCl with NH₃ to form the large area, semi-insulating gallium nitride.

81. The method of claim 42, wherein the growth process comprises reacting gallium chloride with ammonia to form the large area, semi-insulating gallium nitride.

82. The method of claim 42, wherein the growth process comprises an HVPE growth process, and the HVPE growth process is carried out to produce gallium nitride with a dislocation defect density not exceeding 10^7 defects/cm².

83. The method of claim 42, wherein the growth process comprises an HVPE growth process, and the HVPE growth process is carried out to produce gallium nitride with a dislocation defect density not exceeding 10^6 defects/cm².

84. The method of claim 42, wherein the growth process comprises a multiple-stage HVPE growth process.

85. The method of claim 42, wherein the growth process comprises an HVPE growth process, wherein reactants NH₃ and HCl are supplied in a ratio NH₃/HCl that is in a range of from about 2 to about 40.

86. The method of claim 42, wherein the growth process comprises an HVPE growth process, wherein the HVPE growth process is carried out with growth rate in a range of from about 50 to about 250 micrometers per hour, growth temperature in a range of from about 950 to about 1150°C, pressure in a range of from about 25 to about 760 torr, and V/III ratio in a range of from about 2 to about 50.

87. The method of claim 42, wherein the dopant species comprises a transition metal, and the growth process comprises mixing the transition metal with a gallium source, thereby forming a solution of the transition metal impurity in gallium.

88. The method of claim 42, wherein the growth process comprises an HVPE growth process and the dopant species comprises a transition metal, wherein the HVPE growth process comprises reacting the transition metal dopant species with HCl to convert transition metal to gaseous metal chloride.

89. The method of claim 42, wherein the growth process comprises an HVPE growth process including reacting hydrochloric acid with metallic gallium to form gaseous gallium chloride, and reacting the gaseous gallium chloride with ammonia to form said large-area, semi-insulating gallium nitride.

90. The method of claim 89, wherein the step of reacting the gaseous gallium chloride with ammonia is conducted in a growth zone, and the dopant species comprises a

transition metal in the growth zone in a form in which the transition metal is incorporated in the growing gallium nitride.

91. The method of claim 42, wherein the growth process comprises reacting the dopant species with HCl to convert the dopant species into a gaseous chloride.

92. The method of claim 42, wherein the growth process comprises providing a transition metal chloride in a growth zone in which the growth process is conducted.

93. The method of claim 42, wherein the dopant species is derived from a transition metal precursor that is introduced to the growth process.

94. The method of claim 93, wherein the transition metal precursor comprises a metalorganic precursor.

95. The method of claim 94, wherein the metalorganic precursor comprises a bis(cyclopentadienyl) compound of the transition metal.

96. The method of claim 95, wherein the transition metal comprises a metal selected from the group consisting of iron, manganese, cobalt, nickel, chromium and copper.

97. The method of claim 42, wherein the dopant species is delivered by bubbler delivery to the growth process.

98. The method of claim 42, wherein the growth process comprises growing the large-area, semi-insulating gallium nitride on a heteroepitaxial substrate.

99. The method of claim 98, wherein the heteroepitaxial substrate comprises a material selected from the group consisting of sapphire and silicon carbide.

100. The method of claim 98, further comprising removing the heteroepitaxial substrate from the large-area, semi-insulating gallium nitride, to yield free-standing large-area, semi-insulating gallium nitride.

101. The method of claim 100, wherein removal of the heteroepitaxial substrate from the large-area, semi-insulating gallium nitride, comprises a step selected from the group consisting of grinding, chemical etching, dry etching, parting techniques and liftoff techniques.

102. The method of claim 100, wherein removal of the heteroepitaxial substrate from the large-area, semi-insulating gallium nitride, comprises reactive ion etching.

103. The method of claim 100, wherein removal of the heteroepitaxial substrate from the large-area, semi-insulating gallium nitride, comprises in situ removal of the heteroepitaxial substrate at or in the vicinity of growth temperature of the large-area, semi-insulating gallium nitride.

104. The method of claim 100, wherein removal of the heteroepitaxial substrate from the large-area, semi-insulating gallium nitride, comprises fracturing the heteroepitaxial substrate from the large-area, semi-insulating gallium nitride.

105. The method of claim 100, wherein removal of the heteroepitaxial substrate from the large-area, semi-insulating gallium nitride, comprises use of a parting layer between the heteroepitaxial substrate and the large-area, semi-insulating gallium nitride.

106. The method of claim 100, wherein removal of the heteroepitaxial substrate from the large-area, semi-insulating gallium nitride, comprises impinging energy on an interface between the heteroepitaxial substrate and the large-area, semi-insulating gallium nitride, to weaken the interface and cause separation of the heteroepitaxial substrate from the large-area, semi-insulating gallium nitride.

107. The method of claim 42, wherein the large area, semi-insulating gallium nitride is formed as a boule, further comprising forming wafer blanks from said boule.

108. The method of claim 107, wherein the step of forming wafer blanks from said boule comprises sawing wafer blanks from the boule.

109. The method of claim 107, further comprising at least one processing step selected from the group consisting of lapping, polishing and planarization operations.

110. The method of claim 109, wherein the wafer blank after said at least one processing step has a dislocation defect level on a surface thereof that is below 10^6 defects cm^{-2} .

111. The method of claim 42, wherein said dopant species comprises iron, and said large-area, semi-insulating gallium nitride has iron doped therein at concentration in a range of from about 3×10^{16} atoms/ cm^3 to about 7×10^{17} atoms/ cm^3 , as determined by SIMS.

112. The method of claim 42, further comprising fabricating a microelectronic circuitry on and/or in the gallium nitride, wherein the gallium nitride is semi-insulating in an operating temperature regime of said microelectronic circuitry.

113. The method of claim 42, further comprising using the large-area, semi-insulating gallium nitride as a substrate for an electronic device.

114. A method of forming large area, semi-insulating gallium nitride, comprising growing gallium nitride material by a growth process in which donor species in the growing gallium nitride are compensated, by introducing into the growing gallium nitride one or more deep acceptor species in a sufficient amount to compensate the donor species and produce semi-insulating GaN material.

115. The method of claim 114, further comprising maintaining BIC below BIL during the growth process.

116. The method of claim 114, wherein said acceptor species comprises iron, and BIC is below $5.0 \times 10^{17} \text{cm}^{-3}$.